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(54) Title: CIRCULAR METHOD FOR PICKLING COPPER AND COPPER ALLOYS

(57) Abstract

The invention relates to a circular method for pickling copper and copper alloys. So far it has not been possible to pickle copper and copper alloys of different compositions with one pickling solution having the same basic composition. According to the inventive method, a sulfuric ferric sulfate solution with or without peroxodisulfate is used to pickle copper or copper alloys. The spent pickling solution is regenerated in one or more regeneration electrolytic cells which are partitioned by ion exchanger membranes or porous diaphragms. The dissolved copper is cathodically deposited and the ferric sulfate is anodically reoxidized, whereby optionally peroxodisulfate is formed. The regenerated pickling solution enriched with oxidizing agent is fed again to the pickling solution to adjust a predetermined redox potential. The method is suitable for the surface treatment of semi-finished copper and copper-alloy products and articles for removing oxide films and for activating the surface before a surface refinement by electroplating is carried out.

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### **Circular method for pickling copper and copper alloys**

The method concerns a method for the surface treatment of semifinished products and objects of copper and copper alloys for the removal of oxide layers after thermal treatment as well as for activation of the surface prior to surface refinement by electroplating, designated below in summary as "pickling". Copper alloys, which for the most part have very different compositions, also require different pickling methods in order to achieve optimal surface conditions.

Usually, pickling is based on dilute mineral acids, particularly sulfuric acid with addition of oxidation agents such as nitric acid, chromic acid, hydrogen peroxide, iron-III sulfate and peroxodisulfate. The disposal of spent pickling baths presents a great many problems, since compounds which are used for the pickling bath, such as, e.g., chromic acid, pollute the environment, or such compounds are formed during the pickling process, e.g., nitrite and NO<sub>x</sub> when nitric acid is used. Also, such pickling chemicals as chromic acid, iron-III sulfate and peroxodisulfate represent a considerable cost factor and for this reason can only be utilized for special applications.

In order to prevent environmental pollution and/or to minimize the expenditure for pickling chemicals and the disposal of spent pickling solutions according to environmental legislation, pickling methods are particularly preferred today, which completely do away with the use of toxic chemicals and which make possible, insofar as this can be done, a partial or complete closed circuit for the

recovery of dissolved metals and/or regeneration of pickling agent. Thus, methods based on sulfuric acid/hydrogen peroxide are preferably utilized, since the hydrogen peroxide used as the oxidation agent is decomposed with the formation of water and oxygen, and copper can be recovered electrochemically with the reformation of sulfuric acid. However, this method does not supply satisfactory pickling results for all copper materials (e.g., for copper-nickel alloys). Also, the risk of spontaneous decomposition cannot be completely excluded with the use of hydrogen peroxide additions and a completely closed circuit is thus also not possible, since the oxidation agent, hydrogen peroxide, cannot be reformed and must be continually replaced.

A known method, which makes possible a completely closed circuit is the peroxodisulfate recycling method with the use of sulfuric acid pickling solutions, which contain peroxodisulfates as oxidation agents (*Metalloberfläche* 50 (1996) 273). The spent pickling solution is regenerated in regeneration electrolytic cells in such a way that first, the remaining peroxosulfate is reduced by cathodic treatment and the dissolved copper is recovered as a metal, and then the peroxodisulfate is reformed by anodic treatment on anodes of smooth platinum. In different variants of the method, the dissolved copper can be precipitated in compact form completely or partially in an undivided metal-recovery electrolytic cell connected upstream or directly in the cathode spaces of the peroxodisulfate regeneration electrolytic cell partitioned by cation exchanger membranes, as are described, e.g., in DE 4,419,683, and is thus recovered. The dissolved copper can be precipitated completely or partially in the form of metal powder, directly in

the cathode spaces of the peroxodisulfate electrolytic cell and can be discharged by means of a separating device together with the circulating catholyte, supported by periodic flushing-out processes.

The electrochemical formation conditions for peroxodisulfates require the use of anodes of smooth platinum, electrolysis with high anodic current densities, the maintaining of a high total sulfate content in the circulating solution as well as an addition of compounds that increase the potential, e.g., thiocyanates, in order to obtain sufficiently high current yields. The ammonium peroxodisulfate which has been frequently used in the past as the oxidation and pickling agent has been replaced at the present time predominantly by sodium peroxodisulfate for environmental reasons. It has already been proposed to replace the latter completely or partially by the peroxodisulfates of the dissolved metals, e.g., the alloy components zinc or nickel.

These recycling pickling methods based on electrochemically regenerated peroxodisulfates, however, have the disadvantage that the peroxodisulfate hydrolyzes completely or partially to peroxomonosulfate during the pickling process. Thus, peroxomonosulfate is present in the spent pickling solution. This must be completely removed prior to the anodic reoxidation of the peroxodisulfate by cathodic treatment, since it would greatly reduce the current yield due to depolarization of the anode. This is particularly the case if the pickling process requires relatively high contents of peroxodisulfate in the pickling solution and elevated pickling temperatures, which are associated with high losses and thus also with poor economical results. This is particularly

unfavorable if large volumes of pickling solution are required in the pickling process and if the decomposition is additionally accelerated by the presence of catalytically acting metal compounds or metal slurries.

Finally, only insufficient surface qualities can be achieved for a number of copper alloys when pickling is conducted with peroxodisulfate. This particularly concerns copper materials containing tellurium and sulfur as alloy components, in which, coatings of amorphous tellurium or sulfur are formed. Generally speaking, these coatings can be removed sufficiently during the pickling process only by means of an expensive mechanical post-treatment.

Another disadvantage results from the fact that it is not possible to treat the entire assortment of materials of copper and variously composed copper alloys in a pickling bath and obtain uniformly good pickling results just by varying the peroxodisulfate content when the same basic composition of peroxodisulfate pickling solution is used. The redox potential adjusted in the pickling bath lies above 1100 mV (measured against an Ag/AgCl reference electrode) for small contents of peroxodisulfate and decreases to values below 400 mV when peroxodisulfate is absent. The stable adjustment of intermediate values of the redox potential in the pickling bath, which would contribute to improvement of the pickling result for many copper materials, is practically impossible.

The problem that is the basis of the present invention is to find a circular method for pickling copper and copper alloys, with which the above-named disadvantages of the previous peroxodisulfate recycling pickling method can be overcome, and with which the pickling of different copper alloys with different

requirements for the redox potential to be adjusted in the pickling bath can be produced with the same basic composition of the pickling solution that is used.

This problem was solved by the recycling pickling method formulated in the patent claims, in that a sulfuric-acid iron-III sulfate pickling solution is utilized for pickling, with or without peroxodisulfates, and the spent pickling solution is regenerated in one or in several regeneration electrolytic cells partitioned by ion exchanger membranes or porous diaphragms, in that the dissolved copper is precipitated cathodically and the iron-III sulfate is reoxidized anodically and optionally peroxodisulfate is formed, whereby the regenerated pickling solution enriched with oxidation agent is again introduced into the pickling bath for oxidation to a higher state and to establish a pre-given redox potential.

Thus, a base sulfuric-acid pickling solution introduced into the cycle is used, which contains 0.1 to 6 moles/liter sulfuric acid, 0.1 to 0.5 mole/liter copper sulfate and 0.1 to 0.5 mole/liter iron sulfates as well as also up to 2 moles/liter alkali and/or ammonium sulfate and/or sulfates of other dissolved metals, such as, e.g., nickel, zinc, etc.. Therefore, it is necessary to adjust the total sulfate content to values that are above 4 moles/liter as much as possible, in order to obtain sufficiently high current yields. The iron sulfate is present partially or completely as iron-III sulfate in the pickling bath. In the latter case, an excess of peroxodisulfate may also be present. By metering in regenerated pickling solution containing iron-III sulfate and peroxodisulfate, the redox potential in the pickling path (measured against an Ag/AgCl reference electrode), which is determined by the ratio of iron-III sulfate to iron-II sulfate and, if necessary, an

excess of peroxodisulfate, is adjusted to values of 300 mV (only for iron-II sulfate), approximately 700 mV (only for iron-III sulfate) and 1150 mV (excess of peroxodisulfate), adapted to the requirements of the material composition to be pickled.

A peroxodisulfate electrolytic cell, into which a partial flow of the pickling bath to be regenerated is continually metered, is preferably used for regeneration. This partial flow first passes through the cathode spaces for reduction of the residual iron-III sulfate and for precipitation of metallic copper and after this, passes through the anode spaces for reoxidation to iron-III sulfate and for enrichment with peroxodisulfate. It is advantageous that the copper is precipitated in the known way as copper powder and this is discharged and recovered by means of a separating device, e.g., a separating cyclone. The greater the enrichment with peroxodisulfate is, the smaller the partial flow of spent pickling bath will be for introduction by means of regeneration electrolysis. Several liters of spent pickling solution can be oxidized to a higher state and can be brought to the desired composition in the pickling bath with one liter of regenerated pickling solution.

Alternatively, a metal-recovery electrolytic cell that is partitioned by ion exchanger membranes or porous diaphragms may also be utilized for regeneration, e.g., a plate cell with special steel cathodes and anodes of platinized titanium. Cathodically, in addition to the reduction of excess iron-III sulfate, the dissolved copper is precipitated and recovered in compact form, while anodically, iron-III sulfate is reoxidized. With the exclusive use of such a metal-

recovery electrolytic cell as the regeneration electrolysis, however, the pickling bath may only be operated in the range of a redox potential of 300-700 mV, since no peroxodisulfate can be formed as an oxidation agent buffer.

The combination of a metal-recovery electrolytic cell with a peroxodisulfate electrolytic cell has been demonstrated to be a particularly advantageous variant. By recovery of copper powder from the cathode spaces of the peroxodisulfate electrolytic cell and its dissolution in the partial flow of spent pickling bath that has been taken out and cycled for regeneration, first of all, the still-present excess of iron-III sulfate, and optionally of peroxodisulfate, can be decomposed. The principal quantity of copper can be precipitated in compact form and recovered in subsequent passage through the cathode spaces of the metal-recovery electrolytic cell. This occurs with a high current yield, since after pretreatment with copper powder, only small residual quantities of iron-III sulfate are still present, which are reduced at the cathode and are thus in a position to reduce the current yield. Then the pickling solution that has been de-coppered beforehand and is freed of oxidation agent is introduced into the cathode spaces of the peroxodisulfate electrolytic cell. The copper powder precipitated therein and discharged is recovered for pretreatment of the pickling solution to be regenerated. The pickling solution that has been freed of copper except for a residual content of 0.2 to 2 g/l now sequentially passes through the anode spaces of the metal-recovery electrolytic cell and the peroxodisulfate electrolytic cell. Oxidation of the iron-II ions takes place in the metal-recovery electrolytic cell while the enrichment with peroxodisulfate oxidation buffer takes

place in the peroxodisulfate electrolytic cell. After this, the thus-regenerated pickling solution is metered into the pickling bath for reoxidation of the iron-II sulfate formed therein during the pickling process, whereby the preselected redox potential is maintained in the pickling bath.

However, with this combination, other hydrodynamic circuits of the electrode spaces are also possible and can be meaningful. Thus, a larger partial flow of the spent pickling bath can be fed back directly through the anode spaces of the metal-recovery cell to the pickling bath. An enrichment with iron-III sulfate is conducted therein. A smaller partial flow is led sequentially through the cathode spaces of the metal-recovery electrolytic cell and the peroxodisulfate electrolytic cell for removal of copper, and then is enriched with the oxidation buffer, peroxodisulfate, in the anode spaces of the peroxodisulfate electrolytic cell, and thus the pickling bath is adjusted to the necessary redox potential. With this procedure, it is also possible to store the pickling solution enriched with 0.1 to 1 mole/liter peroxodisulfate and thus to raise the redox potential in the pickling bath from a lower level to a higher level for a short time. This may be necessary, e.g., if materials are first pickled, which supply good results in the redox potential range of 500 to 700 mV (iron-III/iron-II region), and then the redox potential range will be changed to above 1100 mV in order to pickle special materials with an excess of peroxodisulfate.

It has been shown that for copper materials containing tellurium and/or sulfur as the alloy component, the adjustment of a redox potential range between 300 and 500 mV, thus in the base solution without excess of oxidation agent,

supplies particularly favorable results, and precipitations of tellurium and/or sulfur on the pickled surface can be avoided. On the other hand, for copper alloys with the alloy components zinc, tin, and/or small quantities of nickel, cobalt, iron, beryllium, lead, phosphorus, zirconium, silver and others, however, without tellurium and sulfur, good results are obtained preferably in the redox potential range between 500 and 700 mV, thus in the iron-II/iron-III range. In particular, for copper alloys with high nickel contents above 20%, it is recommended, however, to establish a higher redox potential between 700 mV (iron-II sulfate is no longer present) and 1150 mV (excess of peroxodisulfate) in the pickling bath in order to achieve a good surface state with sufficiently high pickling rates (all redox potential values measured against an Ag/AgCl reference electrode).

The advantages resulting from the application of the invention can be summarized as follows:

- The closed circuit makes possible the economical use of cost-intensive pickling chemicals such as iron-III sulfate and peroxodisulfate.
- Particularly good pickling results can be achieved by the possible combination of iron-III sulfate and peroxodisulfate.
- When compared with the known peroxodisulfate recycling method without addition of iron sulfate, smaller contents of peroxodisulfate are necessary in order to obtain the same pickling results, whereby smaller decomposition losses and thus better yields are attained.
- The range of application is increased, since very different redox potentials adapted to the different requirements of the material compositions to

be pickled may be adjusted with the same regeneration technology in the pickling bath.

-- It is possible to optimally pickle materials with very different requirements for their pickling conditions without changing the pickling solution, only by varying the metered quantities and/or the hydrodynamic circuit of the different components of the regeneration plant.

### **Examples of application**

#### **Example 1:**

A recycling pickling plant constructed according to the simplified diagram of the method, which is shown in Fig. 1, served for simulation of a closed circuit run for the pickling of copper materials. The pickling of copper materials is conducted in pickling bath 1 with preferred temperatures in the range of 30 to 60°C. The spent pickling solution that is particularly enriched with copper is transferred to the intermediate tank 2 by means of pump P1 in order to be fed from there by means of pump P2 into the electrolytic circuit comprised of metal-recovery cell 3, circulating pump P3 and intermediate vessel 4. The metal-recovery cell is a plate cell with cathodes of copper or special steel and anodes of platinized titanium. The anodes are arranged in pockets of porous plastic materials, which extensively prevent a reoxidation of the iron present in divalent form in the cathode space and in this way assure a sufficiently high current yield of the copper precipitation. Also, the fact that the copper content is enriched only to 4 to 10 g/l, serves for assuring a high current yield with a relatively high current density.

The pickling solution that has been freed of copper beforehand is metered into the catholyte circuit of peroxodisulfate recycling cell 6 by means of metering pump DP1. The catholyte is cycled over the cathode spaces separated by cation exchanger membranes and separating cyclone 5 by means of circulating pump P4. The copper is precipitated in the form of copper powder at the cathodes comprised of impregnated graphite under the necessary conditions of concentration, flow and current density, which are known for this procedure. This powder is fed back to the intermediate tank 2 and is again dissolved in the spent pickling solution, which still contains residual oxidation agent, iron-III sulfate. In this way, all of the dissolved copper is obtained in compact form in the metal-recovery cell and also the current yield of copper precipitation increases, since less residual oxidation agent is reduced cathodically.

A quantity of catholyte corresponding to the volumetric flow metered into the catholyte circuit is transferred to the anode space. Here, iron-II ions are oxidized to iron-III ions and a peroxodisulfate excess is formed as an oxidation agent buffer at the anodes of smooth platinum, while maintaining the known electrolysis conditions that are necessary for this. The thus-regenerated pickling solution reaches collecting tank 8 by means of gas separator 7, and from this collecting tank a quantity is fed into the pickling bath by means of metering pump DP2 such that the necessary redox potential is maintained therein within pre-given limits. The test plant, which was used for the following examples of application, was comprised of a metal-recovery cell at 300 A and a bipolar peroxodisulfate recycling cell at 2 x 300 A.

**Example 2:**

Semifinished copper products were pickled in the pickling bath at approximately 50°C in the same technical plant as in Example 1, whereby an average of 225 g of copper were dissolved hourly in the stationary state. Pickling was conducted with a redox potential of approximately 1100 mV (against an Ag/AgCl reference electrode) in a range, in which all of the iron is present as iron-III sulfate and a small peroxodisulfate excess was established, calculated as sodium peroxodisulfate of 12 g/l. The spent pickling solution discharged from the pickling bath and introduced for regeneration had the following composition:

300 g/l sulfuric acid (SA)

80 g/l sodium sulfate (NaS)

12 g/l sodium peroxodisulfate (NaPS)

10 g/l Fe<sup>3+</sup>

15 g/l Cu<sup>2+</sup>

10 g/l Ni<sup>2+</sup>

Approximately 900 g of copper powder were dissolved in 150 liters of this pickling solution, whereby the excess NaPS was completely reduced and the iron-III sulfate was partially reduced except for a residual content of 5 g/l (as Fe<sup>3+</sup>). The copper content was increased to 21 g/l. Then this solution was electrolyzed at 300 A over 8 h in the metal-recovery cell. 2,250 g of copper were precipitated, and the copper content in the solution was reduced from 21 to approximately 7 g/l. This corresponded to a current yield of copper precipitation

of approximately 79%, and the cell voltage was 4.5 V. The solution thus freed of copper, was comprised as follows:

318 g/l SA

85 g/l NaS

10 g/l Fe<sup>2+</sup>

7 g/l Cu<sup>2+</sup>

10 g/l Ni<sup>2+</sup>

This solution was fed into the catholyte circuit of the peroxodisulfate recycling cell with overflow into the anode spaces at a metering rate of approximately 15 liters/h. A cathodic precipitation of the residual copper in the form of copper powder was produced along with an anodic reoxidation to Fe<sup>3+</sup> ions and an enrichment with peroxodisulfate. The regenerated pickling solution to be metered into the pickling bath was comprised as follows:

280 g/l SA

33 g/l NaS

87 g/l NaPS

10 g/l Fe<sup>3+</sup>

ca. 1 g/l Cu<sup>2+</sup>

10 g/l Ni<sup>2+</sup>

This corresponded to a current yield of 61% relative to the sum of the formed oxidation agents, peroxodisulfate and iron-III sulfate. The 150 liters of regenerated pickling solution obtained in this way were again introduced into the

pickling bath. Thus a total of approximately 2,250 g of copper can again be dissolved, which is enclosed in the process cycle.

### Example 3

A redox potential of approximately 700 mV was adjusted in the same technical plant as in Examples 1 and 2 and with the same pickling solution from Example 2, so that the peroxodisulfate excess was decomposed and thus pickling could be conducted in the redox range of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  system. The spent pickling solution discharged from the pickling and introduced for regeneration was composed as follows:

300 g/l SA

80 g/l NaS

7.5 g/l  $\text{Fe}^{3+}$

2.5 g/l  $\text{Fe}^{2+}$

20 g/l  $\text{Cu}^{2+}$

10 g/l  $\text{Ni}^{2+}$

Approximately 500 g of copper powder were dissolved in 170 liters of this solution for reduction of the principal quantity of iron-III sulfate excess, whereby the copper content was increased to 23 g/l and the  $\text{Fe}^{3+}$  content was reduced to approximately 2-3 g/l.

This solution was electrolyzed for 11 h at 300 A in the metal-recovery cell. 3,230 g of copper were precipitated in this way, corresponding to a current yield of 82.6%. The solution, thus freed of copper, had the following composition:

320 g/l SA

86 g/l NaS

10 g/l Fe<sup>2+</sup>

4 g/l Cu<sup>2+</sup>

10 g/l Ni<sup>2+</sup>

It was introduced into the cathode circuit of the peroxodisulfate recycling cell with overflow into the anode spaces at a metering rate of 17 liters/h. The copper was decreased to less than 1 g/l in the cathode circuit and separated in the form of metal powder. In passing through the anode spaces, the Fe<sup>2+</sup> ions were oxidized and the peroxodisulfate was regenerated. The thus-regenerated pickling solution was composed as follows:

290 g/l SA

45 g/l NaS

74 g/l NaPS

10 g/l Fe<sup>3+</sup>

1 g/l Cu<sup>2+</sup>

10 g/l Ni<sup>2+</sup>

The current yield relative to the sum of the regenerated oxidation agent was again approximately 61%.

The 170 liters of the regenerated pickling solution that were obtained in this way were again metered to the pickling bath in a quantity such that an approximately constant redox potential in the range of 600-700 mV was established therein. Thus again, a total of approximately 3,230 g of copper can be dissolved, which can be contained in the process cycle. As in Example 2, all

of the dissolved copper is recovered by return of the copper powder to the more compact form that can be well used again.

**Example 4:**

The method was conducted as follows in the same technical plant as in Examples 1 to 3 for pickling without oxidation agent, which is suitable, e.g., for copper materials containing tellurium, with redox potentials of approximately 300 mV (against an Ag/AgCl-reference electrode): The completely reduced pickling solution that was depleted of copper and obtained in Example 3 after passing through the previous copper-removal cell was introduced directly into the pickling bath again with disconnection of the peroxodisulfate recycling cell, and copper was dissolved therein until all of the iron-III sulfate was converted to the reduced form in the pickling bath. After reaching the stationary state, a copper content of approximately 20 g/l was adjusted in the pickling bath. 22 liters of this solution were removed from the pickling bath per hour and replaced by the regenerated solution depleted of copper. 176 liters of this solution were electrolyzed in the metal-recovery cell at a current intensity of 300 A over a time of 8 h. A depletion of copper down to 6 g/l was produced. In the stationary state, this corresponds to a copper quantity of 308 g that is dissolved and recovered per hour (current yield of 86.7 %).

**Example 5:**

Figure 2 shows a simplified method diagram for the regeneration of an iron-III sulfate pickling solution without the possibility of formation of

peroxodisulfate as an oxidation agent buffer. The regeneration electrolytic cell is comprised only of a metal-recovery cell 2 partitioned by means of cation exchanger membranes. A spent pickling solution that is depleted of iron-III sulfate and enriched with copper sulfate is metered from pickling vat 1 by means of metering pump DP1 for the anolyte and metering pump DP2 for the catholyte of the metal-recovery cell. Thus the catholyte passes through the cathode spaces 3 and is reduced at cathodes 4 of special steel, whereby the residual iron-III sulfate is converted to iron-II sulfate and the dissolved copper is precipitated in compact form. The catholyte overflow is introduced into anode space 5 together with the partial flow of spent pickling solution transported by means of metering pump DP2. The anode space is formed by a pocket 7 with cation exchanger membranes attached tightly on both sides. The reoxidation to iron-III sulfate is conducted at anode 6 comprised of platinized titanium. The metering quantity is selected such that a fraction of iron-II sulfate is still present in the regenerated pickling solution, in order to obtain sufficiently high current yields. The technical cell was operated with a current intensity of 100 A. The cathodic current density was 150 A/m<sup>2</sup>.

**Example 6:**

An initial pickling solution, which was approximately 3 molar sulfuric acid and contained 0.25 mole/liter iron as sulfate (approximately 14 g/l of iron) was utilized in the same technical plant as in Example 5. This solution was enriched with iron-III sulfate by anodic oxidation and copper materials were pickled with this in the pickling vat. After a run-in phase, a stationary state was obtained, in

which 9.5 liters/h of the spent pickling solution were introduced via the cathode space into the anode space and also 20 liters/h were directly metered into the anode space. Approximately 29.5 liters/h of regenerated pickling solution were discharged from the anode space. A concentration of trivalent iron of 0.075 mole/liter was adjusted in the pickling bath with a copper concentration of 0.25 mole/liter. All iron was present in the divalent form in the catholyte overflowing from the cathode space into the anode space and the copper content was reduced to 0.1 mole/liter. The regenerated anolyte discharged from the anode space and fed back into the pickling bath had a copper concentration of 0.2 mole/liter and a concentration of iron-III ions of 0.15 mole/l (8.4 g/l).

In the stationary operating state, 90.5 g/h of copper were dissolved and again recovered in the regeneration electrolytic cell. The current yield, referred to the copper recovery, was 76.4%. With the obtained cell voltage of 4.2 V, a specific electrical energy consumption of 4.6 kWh/kg of copper resulted. When pure copper materials were used, a stripping rate of approximately 0.5  $\mu\text{m}/\text{min}$  was measured in the pickling bath at 50°C.

#### **Example 7:**

An industrial pickling bath contained approximately 20  $\text{m}^3$  of a pickling solution, which was composed analogously to that of Example 2. The redox potential was adjusted to 1150 mV (against Ag/AgCl) by metering in the regenerated pickling solution, a potential that is suitable for the pickling of copper-nickel alloys. Five sheets that were highly oxidized due to prior hot rolling and of dimensions 7000 x 300 x 10 mm (length x width x height) of the alloys

CuNi10Fe1Mn and CuNi30Mn1Fe were positioned individually on edge in an acid-resistant pickling frame and dipped into the pickling solution preheated to approximately 60°C. The pickling solution was placed in motion by intense bubbling in of air in order to support the pickling process. After approximately 30 min of pickling time, the pickling frame was raised from the pickling solution by means of a crane, and after draining off the pickling solution, the sheets were first cleaned by means of a spray pickling solution to remove still loosely adhering oxides in places and then rinsed first with cold water and then with hot water (approximately 90°C). Then the bright metal pickled surface was dried uniformly without formation of water spots. The sheets could be removed from the frame and further processed.

**Example 8:**

Semifinished products of copper-tellurium-phosphorus alloys were pickled in the same industrial pickling bath as in Example 7. A pickling solution composed according to Example 4 and reduced after passing through the prior copper-removal cell was utilized for this purpose. Pickling was conducted with a redox potential adjusted in the pickling solution of 300 mV at 60°C. Extruded flat bars of dimensions 9000 x 300 x 10 mm (length x width x height) were made up into bundles of approximately 4000 kg with the use of spacers and immersed into the pickling solution by means of a crane. After a pickling time of approximately 15 min, the bundle was removed from the pickling solution and after draining, was cleaned by means of the spray pickling solution and then rinsed with cold and hot water. After the hot-water rinse, the shiny metal surfaces of the extruded

bars were dried uniformly without formation of water spots. The extruded bars could be detached from one another and further processed.